KINETICS OF PARTLY DIFFUSION-CONTROLLED REACTIONS IV: ARTEFACTS IN SENSITIZED PHOTOREACTIONS

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Summary

Analysis of the measurement of the quantum yield φ of diffusion-controlled energy transfer of an electronically excited molecule A^* towards an acceptor B leads in principle to the determination of the lifetime τ_0 and the quantum yield ϕ_0 of formation of A^*. However, for short lifetimes of the donor A^*, the classical linear expression between $1/\varphi$ and $1/[B]$ is no longer valid and a more accurate relation with non-stationary diffusional terms and static sensitization must be used; this relation leads to calculated τ_0 and ϕ_0 values which are quite different from those obtained using the classical linear expression. Good agreement between our kinetic model and experimental results was obtained.

1. Introduction

Theories of diffusion-controlled reactions have already received considerable attention [1 - 9]. Various experimental verifications have been reported, involving in particular photochemical and photophysical quenching (see for example refs. 7 - 9) and sensitization (see for example refs. 10 - 19). In three recent papers [7 - 9] we have described and verified two simplified kinetic models in which competition between the kinetic reaction and the diffusion of the reagents can occur. Experimental studies have been especially concerned with quenching of fluorescence, and we have reported an application of the kinetic model described in ref. 7 to sensitized reactions. In fact, we shall consider that the "chemical" rate constant k_c is almost infinite for a collisional energy transfer (Dexter type). When the lifetime of the excited state of the donor is short (of the order of nanoseconds in usual solvents), deviation from the classical linear representation of $1/\varphi$ *versus* $1/[B]$ (where φ represents the sensitized quantum yield and [B] is the aver-

age concentration of the acceptor or quencher) might be expected to occur because of static sensitization and non-stationary diffusional phenomena.

2. Kinetic model for sensitized reactions

A^* is an electronically excited molecule which can transfer its electronic energy to B. Let us consider [7] two distinct volumes in the reacting system centred on the molecule A^* towards which molecules B diffuse.

(1) The first is a reaction zone between the radii σ and σ' where σ defines the distance of closest approach. Within this zone the reaction is assumed to occur with essentially an infinite rate.

(2) The second is an external volume ($r > \sigma'$) in which only diffusion occurs.

Under these conditions the value of the apparent rate constant is given by

$$k_a(t) = 4\pi N\sigma'D \left\{1 + \frac{\sigma'}{(\pi Dt)^{1/2}} \right\} \tag{1}$$

where D is the sum of the diffusion coefficients of A^* and B, and N is the Avogadro number.

2.1. Probability of sensitization
2.1.1. Probability of sensitization at time t = 0
If the volume V_1 between σ and σ' is $\frac{4}{3}\pi(\sigma'^3 - \sigma^3)$, then the probability p_s of static transfer is given by

$$p_s = 1 - \exp(-NV_1[B]) \tag{2}$$

2.1.2. Probability of sensitization at time greater than zero (t > 0)
If k is the rate constant for the disappearance of A^* in the absence of B, then the variations of the concentration of A^* with time can be described by relation (3):

$$[A^*] = [A^*]_{t=0} \exp(-NV_1[B]) \exp\left[-kt - k_0[B]t \left\{1 + \frac{2\sigma'}{(\pi Dt)^{1/2}}\right\}\right] \tag{3}$$

where $k_0 = 4\pi N\sigma'D$ and it is assumed that $k_c \gg k_0$.

Under these conditions the value of the rate of energy transfer is

$$r = k_a(t)[B][A^*]$$

where [B] is the average concentration of the acceptor or quencher. The probability p_d of dynamic energy transfer is

$$p_d = \frac{1}{[A^*]_{t=0}} \int_0^\infty r \, dt$$

leading to

$$p_d = \exp\left(-NV_1[B]\right) \left\{1 - \frac{I(\lambda)}{1 + k_0\tau_0[B]}\right\} \tag{4}$$

where $\tau_0 = 1/k$ is the natural lifetime of A^* in the absence of B, where

$$\lambda = \frac{2}{\pi^{1/2}} \frac{k_0\tau_0[B]}{(1 + k_0\tau_0[B])^{1/2}} \frac{\sigma'}{(D\tau_0)^{1/2}}$$

and where

$$I(\lambda) = \int_0^\infty \exp\left(-u - \lambda u^{1/2}\right) du$$

$$= 1 - \frac{1}{2}\lambda\pi^{1/2} \exp\left(\frac{\lambda^2}{4}\right) \text{erfc}\left(\frac{\lambda}{2}\right) \tag{5}$$

2.1.3. Probability of transfer and the quantum yield of the transfer

Let

$$p = p_s + p_d = 1 - \frac{I(\lambda) \exp\left(-NV_1[B]\right)}{1 + k_0\tau_0[B]}$$

Assuming that ϕ_0 is the quantum yield of formation of A^*, the quantum yield of energy transfer ($\varphi = p\phi_0$) is expressed by the simple relation

$$\varphi = \phi_0 \left\{1 - \frac{I(\lambda) \exp\left(-NV_1[B]\right)}{1 + k_0\tau_0[B]}\right\} \tag{6}$$

2.2. Linear representations of $1/\varphi$ versus $1/[B]$

For large values of τ_0 (*i.e.* 1 μs), the transfer is almost total for very low concentrations of acceptor (below 10^{-5} mol l^{-1} in usual solvents) and relation (6) leads to

$$\varphi \approx \phi_0 \left(1 - \frac{1}{1 + k_0\tau_0[B]}\right) \tag{7}$$

which is the classical linear representation

$$\frac{\phi_0}{\varphi} \approx 1 + \frac{1}{k_0\tau_0} \frac{1}{[B]} \tag{8}$$

This relation is generally used; the known value of φ, measured either using a photoreaction (see for example ref. 10) or using a phosphorescence study (see for example ref. 18), leads to values of ϕ_0 and τ_0.

However, for larger values of [B], which are necessary for shorter values of τ_0 (*i.e.* of the order of nanoseconds), $I(\lambda)$ and $\exp\left(-NV_1[B]\right)$ may be different from unity, and deviations from this classical representation should be observed.

2.2.1. Expansion in a Taylor series for low concentrations of B

Under these conditions

$$I(\lambda) \approx 1 - \frac{k_0\tau_0[\text{B}]}{1 + k_0\tau_0[\text{B}]} \frac{\sigma'}{(D\tau_0)^{1/2}} + \dots$$

and

$$\exp\left(-NV_1[\text{B}]\right) \approx 1 - NV_1[\text{B}] + \dots$$

leading to

$$\frac{\phi_0}{\varphi} \approx \left\{1 + \frac{NV_1}{k_0\tau_0} + \frac{\sigma'}{(D\tau_0)^{1/2}} \frac{1}{(1 + k_0\tau_0[\text{B}])^{1/2}}\right\}^{-1}\left(1 + \frac{1}{k_0\tau_0[\text{B}]}\right) \qquad (9)$$

If the concentration of B is not too high this relation can lead to a linear relation similar to relation (8). If $k_0\tau_0[\text{B}] \ll 1$, then

$$(1 + k_0\tau_0[\text{B}])^{1/2} \approx 1 + \frac{k_0\tau_0[\text{B}]}{2}$$

leading to

$$\frac{\phi_0}{\varphi} \approx \left\{1 + \frac{NV_1}{k_0\tau_0} + \frac{\sigma'}{(D\tau_0)^{1/2}}\right\}^{-1} \times$$

$$\times \left[1 + \frac{\sigma'/(D\tau_0)^{1/2}}{2\{1 + NV_1/k_0\tau_0 + \sigma'/(D\tau_0)^{1/2}\}} + \frac{1}{k_0\tau_0} \frac{1}{[\text{B}]} + \dots\right] \qquad (10)$$

All other terms in this expansion can be neglected. This relation can only be applied in the case of sufficiently low values of [B], as long as $k_0\tau_0[\text{B}]$ is smaller than unity. However, under these conditions φ is also much smaller than unity and generally not accessible to experimental observation. As is shown in Fig. 1, the application of relation (10) for larger values of [B] leads to erroneous values.

2.2.2. Expansion in a Taylor series for large concentrations of B

This expansion is only possible for values of $\exp\left(-NV_1[\text{B}]\right)$ almost equal to unity (if $V_1 \approx 0$, $\phi_0/\varphi = 1$).

Taking into account

$$I(\lambda) \approx \frac{\pi}{4} \frac{1 + k_0\tau_0[\text{B}]}{(k_0\tau_0[\text{B}])^2} \frac{D\tau_0}{\sigma'^2}$$

then

$$\frac{\phi_0}{\varphi} = 1 + \frac{\pi}{4} \frac{D\tau_0}{\sigma'^2} \frac{1}{(k_0\tau_0)^2} \frac{1}{[\text{B}]^2} + \dots \qquad (11)$$

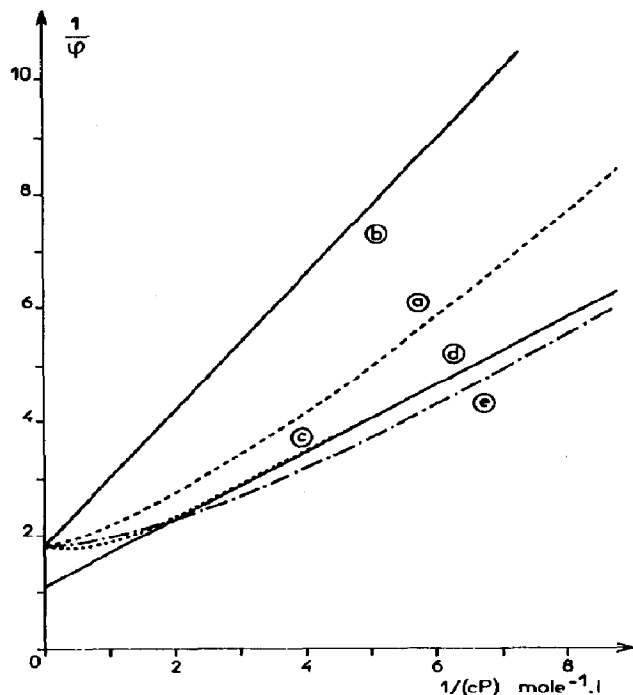Figure 1 represents a qualitative utilization of these various relations.

Fig. 1. Theoretical variations of $1/\varphi$ with $1/[cP]$ where $[cP]$ is the concentration of cis-1,3-pentadiene ($\sigma = 6$ Å, $\tau_0 = 0.15$ ns, $\phi_0 = 0.55$, $D = 1.1 \times 10^{-5}$ cm^2 s^{-1}). Curves for $1 - NV_1 = 0$ mol^{-1} l: a, calculated using relation (7); b, calculated using relation (8); c, calculated using relation (9); d, calculated using relation (10). Curve for $2 - NV_1 = 1$ mol^{-1} l: e, calculated using relation (6).

2.3. Importance of NV_1 and $\sigma'/(D\tau_0)^{1/2}$ for energy transfer measurements

For most of the studies reported on singlet–singlet energy transfer [7, 9, 20 - 24] values of σ' around 10 Å (± 1 Å) have been reported. But σ is generally about 6 Å. Under these conditions NV_1 is about 1 mol^{-1} l. For low viscosity solutions and for excited molecules with lifetimes greater than 10 ns, we can neglect static sensitization and non-stationary diffusional effects. However, these effects can intervene when large concentrations of acceptor are required, e.g. to prove by energy transfer measurements the existence of an excited state with a very short lifetime (i.e. $\leqslant$ 1 ns).

3. Application to experimental data

In recent papers Wagner and coworkers [10, 11] have shown the existence of several triplet states for aromatic ketones such as o-methylaceto-phenone and 4-benzoyl-piperidines. They used the classical technique of energy transfer from these excited states to cis-1,3-pentadiene (cis-piperylene (cP)). The yields of cis–trans isomerization of the diene were corrected for

high concentrations, in agreement with results of Hurley and Testa [13] (see Appendix A).
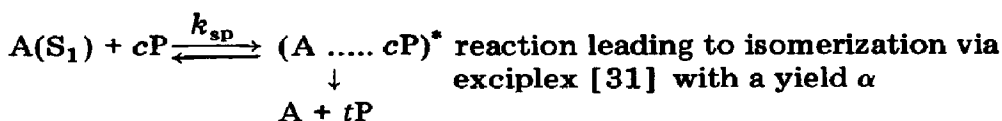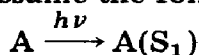
As reported elsewhere, to understand our own results on the photochemistry of benzocyclononenones [25, 26], where excited triplet states could intervene, we have also used this same technique.

3.1. Validity of the technique

When 1,3-pentadiene is used as a quencher B, it is generally assumed that only triplet states generate isomerization of B, although it is well known that singlet states can be quenched by large concentrations of 1,3-pentadiene [27 - 31].

In order to determine if singlet states could isomerize the diene in these inhibition experiments, we studied the sensitization of cis-1,3-pentadiene by acetone by measuring the influence of the concentration of the acceptor on both the sensitization quantum yield and the fluorescence of acetone. Acetone is useful for such experiments since most aromatic ketones do not fluoresce.

The results obtained, corresponding to the variations of $0.55/\varphi_i \approx 1/\varphi$ with $1/[cP]$ (where φ_i is the quantum yield of isomerization, 0.55 is the cis → trans isomerization yield for 1,3-pentadiene and $[cP]$ is the concentration of cis-1,3-pentadiene), must fall between two limiting curves: one for a reaction which is totally sensitized simultaneously by singlet and triplet states of the donor; the other for a reaction which is only sensitized by triplet states of the donor. By taking into account the lifetime τ_0 of the triplet state of acetone in solution in the fluorescence quenching measurements for this compound, we can calculate the theoretical expressions $1/\varphi$ versus $1/[cP]$ if we assume the following sensitization mechanism:

$$A \xrightarrow{h\nu} A(S_1)$$

$$A(S_1) \xrightarrow{k_{S_1}} \ldots \quad \text{fluorescence, radiationless transitions etc.}$$

$$A(S_1) \xrightarrow{k_{ST}} A^* \text{ or } A(T_1) \text{ intersystem crossing transition}$$

$$A(S_1) + cP \underset{\longleftarrow}{\overset{k_{sp}}{\rightleftharpoons}} (A \ldots cP)^* \quad \text{reaction leading to isomerization via}$$
$$\downarrow \qquad \text{exciplex [31] with a yield } \alpha$$
$$A + tP$$

$$A^* \xrightarrow{k} A \qquad \text{relaxation to ground state, photochemistry etc...}$$

$$A^* + cP \xrightarrow{k_a(t)} A + P^* \quad \text{energy transfer}$$

$$P^* \rightarrow cis\text{-P or } trans\text{-P} \qquad \text{isomerization}$$

$$\phi_i \approx \left(\alpha k_{sp}[cP] + 0.55 k_{ST} \frac{k_0[cP]}{k + k_0[cP]} \right) \frac{1}{k_{S_1} + k_{ST} + k_{sp}[cP]} \tag{12}$$
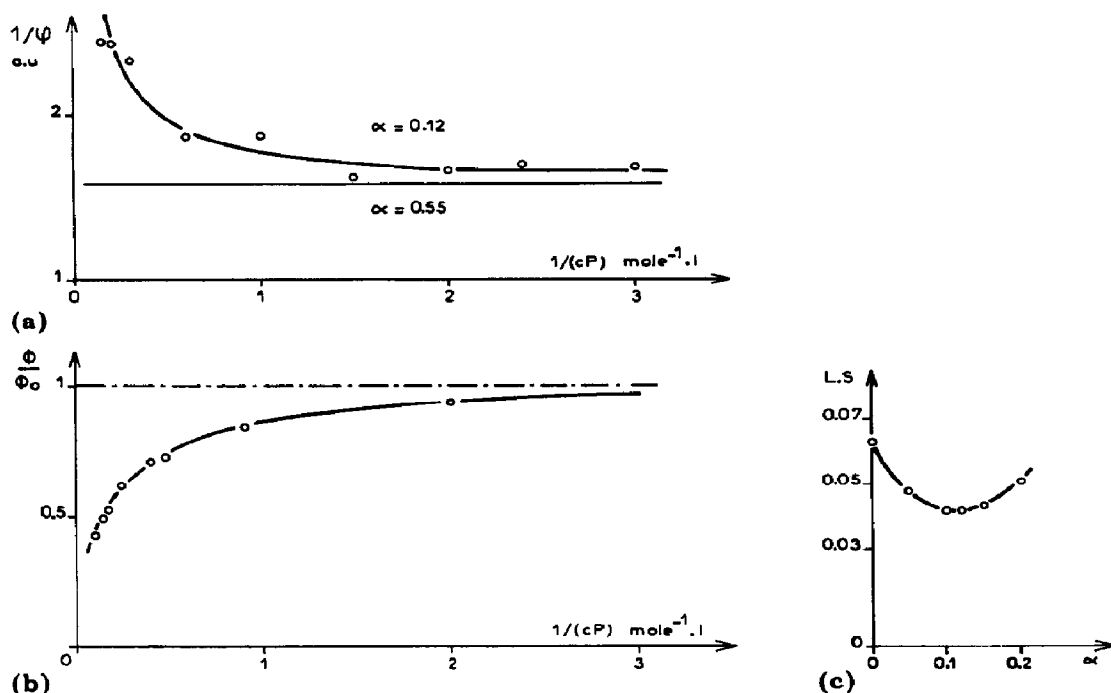
Fig. 2. Sensitization of the isomerization of cis-1,3-pentadiene by acetone $(0.77 \text{ mol } l^{-1})$ in benzene: (a) corrected variation of $1/\varphi$ with $1/[cP]$; best-fitting curve for $\alpha = 0.12$; (b) variation of the ratio of the quantum yield ϕ of fluorescence in the presence of cP to the quantum yield ϕ_0 of fluorescence in the absence of cP with $1/[cP]$; (c) variation of the least-squares fit between experimental and calculated curves (minimum for $\alpha = 0.12$).

The experimental results are shown in Fig. 2. They are in agreement with an α value close to zero; this means that practically only the triplet state leads to cis–trans isomerization[†]. In general, the existence of a possible deactivation of the singlet state by the 1,3-pentadiene must be considered. This might be responsible for wrong interpretations.

3.2. Analysis of some results obtained by Wagner and coworkers

Of the ketones which were studied by these authors [10 - 12] using the described technique, we have reinvestigated 8-methyl-1-tetralone and o-methylacetophenone theoretically and experimentally.

Using the model introduced in Section 2, we plotted in Fig. 3 $1/\varphi$ versus $1/[cP]$ for 8-methyl-1-tetralone, in which ϕ_0 and τ_0 were the best-fitting calculated values. Taking ϕ_0 and τ_0 values from the linear relation (8) leads to a different result, which confirms the results reported in Fig. 1. The

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[†]Variations of α from 0 to 0.2 lead to only small modifications of the least-squares fit corresponding to the deviations between the calculated curve and the experimental data.
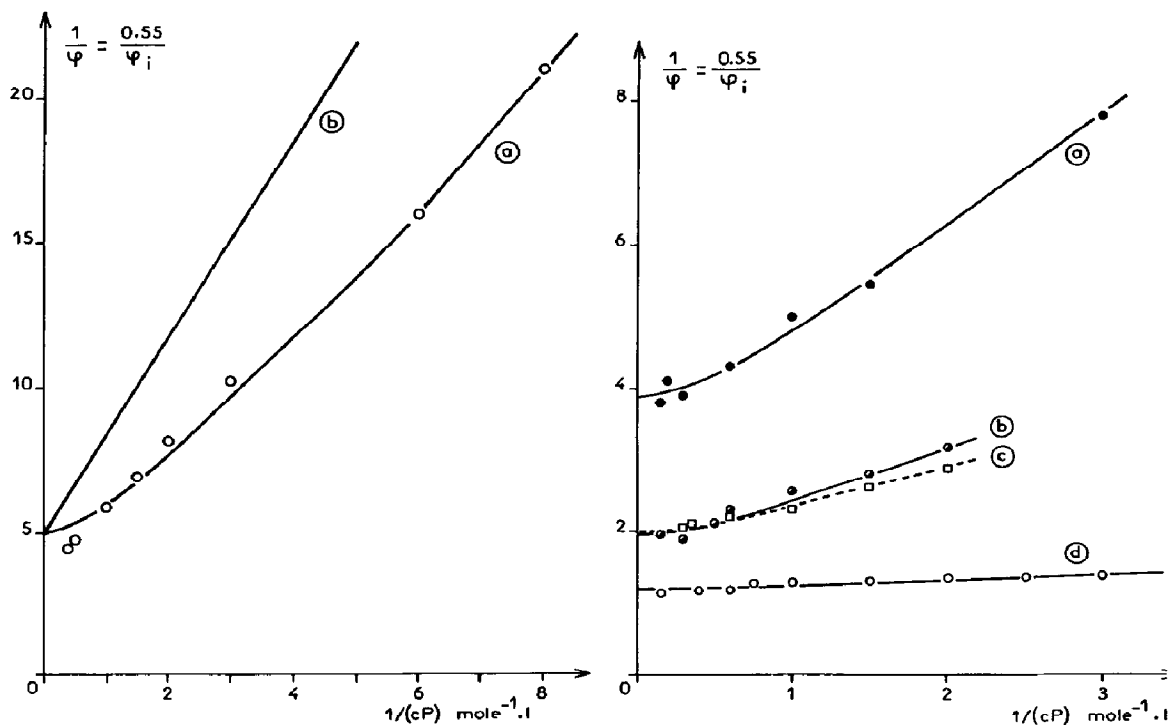
Fig. 3. Variations of $1/\varphi$ with $1/[cP]$ using results for 8-methyl-1-tetralone from Wagner and Chen [10] : a, best-fitting curve ($NV_1 = 0$ mol^{-1} l, $\tau_0 = 0.295$ ns, $\phi_0 = 0.20$); b, calculated straight line using τ_0 and ϕ_0 values from curve a (relation (8)).

Fig. 4. Experimental results and best-fitting curves: a, o-methylbenzocyclononenone (5 × 10^{-2} mol l^{-1}) in benzene at 25 °C; b, o-methylacetophenone (5 × 10^{-2} mol l^{-1}) in benzene at 8 °C; c, o-methylacetophenone (5 × 10^{-2} mol l^{-1}) in pentane at 8 °C; d, benzocyclononenone (5 × 10^{-2} mol l^{-1}) in benzene at 25 °C. (See Table 1.)

number of experimental measurements and their quality, including corrections and determination by vapour phase chromatography, do not allow observation of all the kinetic parameters of the system. In this case, as for all the sensitized reactions studied, we assumed that D was a constant (approximately 1.1×10^{-5} cm^2 s^{-1} for a benzene–1,3-pentadiene mixture [32]) and that σ was about 6 Å[†]. Under these conditions the fitting method of Rosenbrock [33] leads to the results presented in Table 1 for 8-methyl-1-tetralone and o-methylacetophenone.

For the latter compound the experiment shows the presence of two triplet states for the same compound, one with long lifetime and one with very short lifetime, in agreement with the results of Wagner and Chen [10]. However, the quantitative determinations of ϕ_0 and τ_0 are different because of the kinetic model described.

[†]Then $k_0 \approx 5 \times 10^9$ mol^{-1} l s^{-1}, as used by several authors [10].

TABLE 1

Ketone[a]	Temperature (°C)	Solvent	τ_0[b] (ns)	ϕ_0[b]	τ_0 (ns)	ϕ_0	NV_1 (mol⁻¹ l)	Reference
8-Methyl-1-tetralone	22	Benzene–1,3-pentadiene	0.3	0.28	0.295	0.20	0.0	10
o-Methylacetophenone	22	Benzene–1,3-pentadiene	0.48[c]	0.57[c]	–[d]		0.0	10
o-Methylacetophenone	8	Benzene–1,3-pentadiene	0.57	0.54	0.26	0.51	0.0	This work
o-Methylacetophenone	8	Pentane–1,3-pentadiene	0.50	0.51	0.23[e]	0.49[e]	0.0	This work
Benzocyclononenone	25	Benzene–1,3-pentadiene	3.97	0.84	2.05[f]	0.83	0.0	This work
o-Methylbenzocyclononenone	25	Benzene–1,3-pentadiene	0.69	0.21	0.395	0.26	0.0	This work

[a]Concentration, 5×10^{-2} M.
[b]Calculated using relation (8).
[c]Value for short lifetime triplet state.
[d]The results reported in Fig. 1 of ref. 10 did not allow the calculation.
[e]2×10^{-5} cm² s⁻¹ was taken for D for pentane–1,3-pentadiene mixtures [32].
[f]This value is imprecise because of the low concavity of the curve $1/\varphi$ vs. $1/[cP]$.

3.3. Analysis of our experimental results

In comparison with acetone ($\tau_s \approx 1.7$ ns [31]), the lifetimes of singlet states of the four molecules we studied are probably very short in view of the near-zero fluorescence quantum yields. It can be assumed that to a good approximation the singlet state is not quenched by 1,3-pentadiene. We used our model to determine the quantum yield of formation of the short-lived triplet state and its lifetime (see Table 1). The experimental results are in good agreement with the calculated curves (see Fig. 4).

3.4. Limitations of the described model

The study of sensitized reactions with very short lifetime donors ($\tau_0 \lesssim 1$ ns) implicates the use of large concentrations of acceptor, *e.g.* 1,3-pentadiene; under these conditions it is not possible to investigate the influence of viscosity on the apparent rate constant. However, use of a high pressure cell (up to 5000 bar) which will allow a variation of viscosity without modification of the solvent is an attractive possibility and such experiments are contemplated.

4. Conclusions

Except for the limitations introduced in Section 3.4, there is good agreement between our experimental results and the diffusional model described in Section 2. In particular we observe a different result for NV_1 values from those observed for diffusion-controlled reactions of singlet–singlet energy transfer (*i.e.* $NV_1 \approx 1$ mol^{-1} l). In one limit a large NV_1 value indicates an attractive potential between the excited molecule and the quencher. At the opposite extreme, for the reactions described here NV_1 is close to zero indicating the absence of an attractive potential.

If the energy transfer reaction is really diffusion controlled (see Section 3.4), then we would have an example of a reaction for which no static quenching (or sensitization) would occur.

Acknowledgment

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Appendix A

Experimental section

Materials

Benzene, pentane and cyclohexane (Fluka, UV spectroscopic grade) were used without further purification. *cis*-1,3-Pentadiene (Fluka) was distilled over hydroquinone before use. It generally contains 1.1% of *trans*-1,3-pentadiene (gas chromatographic analysis). Acetone (Merck, Uvasol), 2-methylacetophenone (Fluka) and benzophenone (Fluka) were used without further purification. Benzocyclononenone and *o*-methylbenzocyclononenone were prepared by arynic addition following the general procedure of Caubere [A1].
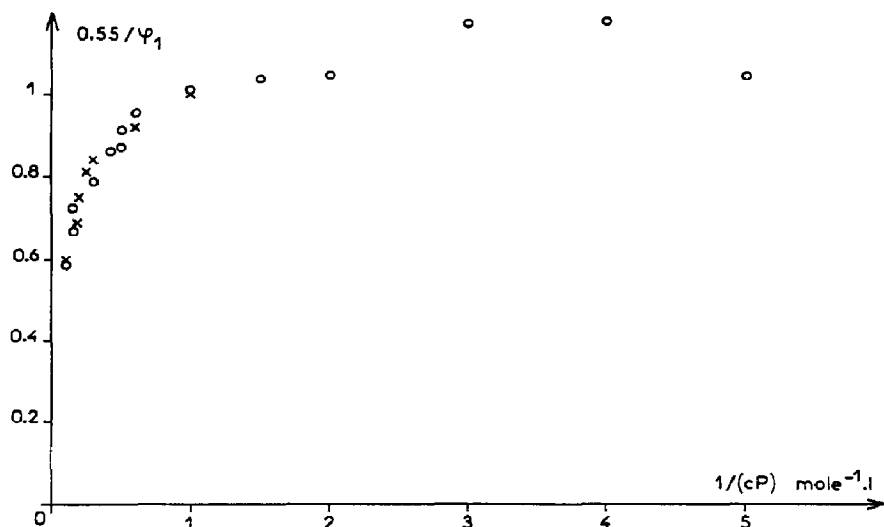
Fig. A1. Influence of [cP] on the yield of isomerization from cP to tP: ×, results from Hurley and Testa [A3]; ○, results from this work.

Analysis

Fluorescence quenching of acetone. Fluorescence spectra were recorded on a Jobin–Yvon JY 3 spectrofluorimeter and were corrected for background emission.

General procedure for measuring 1,3-pentadiene isomerization. Samples were degassed three times in freeze–pump–thaw cycles.

Irradiations were performed with an Osram HBO 500 high pressure mercury lamp. An MTO filter was used to isolate the 366 nm line and a $CuSO_4/NiSO_4$ filter was used to isolate the 313 nm line. The light intensity was determined by uranyloxalate actinometry [A2].

The concentration of *trans*-1,3-pentadiene produced during irradiations was determined with a Carlo-Erba Model 180 chromatograph equipped with a flame ionization detector and a 3 m × $\frac{1}{8}$ in column of 25% β,β'-oxydipropionitrile on spherosil at 40 °C. Irradiation times were selected to give a 2 - 6% isomerization yield.

Correction of data

We reinvestigated the sensitized *cis–trans* isomerization of *cis*-1,3-pentadiene by benzophenone (2×10^{-2} mol l^{-1}) in benzene at high concentrations of diene (above 1.0 mol l^{-1}). Our data are summarized in Fig. A1; the results of Hurley and Testa [A3] are included for comparison.

We corrected the results obtained for the other ketones by taking into account the enhanced isomerization effect for high concentrations of diene.

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